

The question of paramagnetic species in complexes of iodine with certain amines has been discussed elsewhere.^{18, 19}

Inductive Effects in para-Substituted Phenyl Methyl Sulfides. The chemical shifts of a series of sulfides of the type $\text{CH}_3\text{SC}_6\text{H}_4\text{Y}$ in carbon tetrachloride at 25° are presented in Table IV. The chemical shift δ_{free} refers to the proton shift of the $-\text{SCH}_3$ group in carbon tetrachloride solution containing 2% sulfide (by weight), and $\delta_{2\%I_2}$ refers to the methyl proton shift of the sulfide in a carbon tetrachloride solution containing 2% sulfide and 2% iodine (by weight).

The values of the equilibrium constants, K_N , for the sulfides other than *p*-methoxyphenyl methyl sulfide were obtained from a Hammett plot.²⁰ The value of ρ , -2.6 , was selected from a plot of $\log(k/k_0)$ vs. σ for the hydrolysis of a series of *para*-substituted aryl chloromethyl sulfides in aqueous acetone,²¹ where the dependence of the rate constant for hydrolysis upon electron density around the sulfur atom would be expected to be approximately the same as the dependence of the equilibrium constant for complex formation with iodine. The value of ρ for the acid dissociation of thiophenol and substituted thiophenols is $+2.578$.²² The value of σ for the $-\text{NO}_2$ group *para* to divalent sulfur was found²² to be $+1.00$, and this value is used in the present study. The "association shifts" were

(18) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

(19) D. N. Stamires and J. Turkevich, *J. Am. Chem. Soc.*, **85**, 2557 (1963).

(20) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

(21) F. G. Bordwell, G. D. Cooper, and H. Morita, *J. Am. Chem. Soc.*, **79**, 376 (1957).

(22) F. G. Bordwell and H. M. Anderson, *ibid.*, **75**, 6019 (1953).

obtained by calculating the fraction complexed using the values of K_N from the Hammett plot and extrapolating the chemical shift to a proton fraction of unity.

The Hammett plot would be expected to give only a rough correlation for the measured chemical shifts extrapolated to a mole fraction of unity since errors in measurements would result in large errors in the extrapolation. The agreement among the various substituted sulfides is good considering that K_N changes by a factor greater than 200 while the "association shifts" vary only by a factor of 2. This seems to indicate that the "association shifts" are the same or nearly the same for the sulfides studied and that the variation in the values of $\delta_{\text{free}} - \delta_{2\%I_2}$ arise mainly from differences in the equilibrium constants.

A Hammett plot for the association of iodine and *para*-substituted aryl selenides was linear with a ρ -value of -0.7 .²³

From the variation in δ_{free} for the sulfides, it is evident that δ_{free} correlates well with the electron-withdrawing power of the substituted group; the strongest electron-withdrawing group causes the largest downfield shift for the methyl protons.

Acknowledgments. D. W. L. expresses appreciation for a Woodrow Wilson Fellowship, a Fellowship from the Lubrizol Corp., and a predoctoral fellowship from the Division of General Medical Sciences, United States Public Health Service. We thank the Northwestern University Computing Center for providing computer time. The research upon which this report is based was partially supported by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center.

(23) J. D. McCullough and B. A. Eckerson, *ibid.*, **73**, 2954 (1951).

Halogen Complexes. II. The Types and Mean Lifetimes of Complexes Formed by Iodine and 2,4,6-Trimethylpyridine

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The system containing iodine and 2,4,6-trimethylpyridine in mixtures of nitrobenzene and carbon tetrachloride was studied by *n.m.r.* Evidence is presented for this system containing two types of complexes, $\text{C}_8\text{H}_{11}\text{N}\cdot\text{I}_2$ and $[(\text{C}_8\text{H}_{11}\text{N})_2\text{I}]^+\text{I}_3^-$. The amount of the latter type of complex formed in solution was found to depend upon the dielectric constant of the solvent. The Bloch equations were modified to apply to a three-site case, $A \rightleftharpoons B \rightleftharpoons C$, in which there is no direct exchange between sites *A* and *C*, and were solved after assuming that the mean time of a nucleus in site *C* before exchange is much shorter than in site *A*. The resulting expression was used to measure

the rates of exchange of the ionic complex using the *n.m.r.* absorption line shapes and chemical shifts.

Introduction

Complexes of iodine with amines have been studied² by spectroscopic methods and also by X-ray methods in the case of the more stable complexes. These methods make possible the determination of thermodynamic variables, equilibrium constants, and the

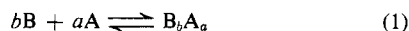
(2) (a) For reviews see L. J. Andrews and R. M. Keefer, *Advan. Inorg. Chem. Radiochem.*, **3**, 91 (1961); G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) O. Hassel, *Mol. Phys.*, **1**, 241 (1958).

(1) Alfred P. Sloan Research Fellow.

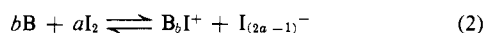
structure of the complexes in the solid state. However, a more thorough understanding of the nature of the complexes might be gained from a study of their mean lifetimes in solution since the complexes are undergoing rapid exchange in solution. For this reason, the present investigation was undertaken.

Theoretical

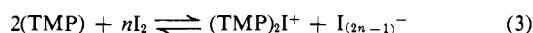
Equilibrium Constants. Consider the interaction between a weak Lewis acid and a weak Lewis base



If B is an amine and A is iodine, the interaction is relatively strong and might be expected to be of the type³



Anticipating the interaction between 2,4,6-trimethylpyridine (TMP) and iodine in nitrobenzene solution, one may write



It is found that in this system a second type of interaction between TMP and iodine is also present



Two equilibrium expressions may now be written for the two separate equilibria

$$K_1 = \frac{C_1^2(A + B + S - nC_1 - C_2)^n}{(B - 2C_1 - C_2)^2(A - nC_1 - C_2)^n} \quad (5)$$

$$K_2 = \frac{C_2(A + B + S - nC_1 - C_2)}{(B - 2C_1 - C_2)(A - nC_1 - C_2)} \quad (6)$$

where A , B , and S refer to the number of moles of acid, base, and solvent, respectively, present in the absence of complex formation; C_1 and C_2 refer to the number of moles of complexes of the types $(\text{TMP})_2I^+$ and $(\text{TMP})I_2$, respectively, present after equilibrium has been established, and K_1 and K_2 are the mole fraction (m.f.) equilibrium constants.

Equations 5 and 6 may be used to obtain the amounts of each type of complex present in a solution containing TMP and iodine if K_1 and K_2 are known. Under certain conditions of concentration and temperature, the n.m.r. spectrum of a solution of TMP and iodine shows two peaks for the α -methyl protons. These two peaks are suitable for the determination of K_1 by the following procedure.

One of the two peaks observed for the α -methyl protons may be attributed to $(\text{TMP})_2I^+$, and the other to $(\text{TMP})I_2$ and free TMP rapidly exchanging. These assignments will be justified later in this report. The areas under the two peaks are proportional to the relative amounts of $(\text{TMP})_2I^+$ and $[(\text{TMP})I_2 + \text{free}$

TMP], which lead to the determination of values for C_1 and $(B - 2C_1)$.

The value of C_2 may then be calculated from eq. 6 provided that K_2 and n are known. The calculations outlined in this paragraph were carried out for each reasonable value of n and also for TMPI^+ as well as $(\text{TMP})_2I^+$. The best over-all fit of the data was obtained by assuming the form $(\text{TMP})_2I^+$ and $n = 5$. The reported value of the equilibrium constant for the analogous system, pyridine-iodine,⁴ was used as the value of K_2 in the present calculations. The values of K_2 at the various temperatures employed were calculated using the reported⁴ value of ΔH . After calculating the value of C_2 , K_1 may be determined by rearranging eq. 5 to the form

$$\frac{K_1(A - nC_1 - C_2)^{n-4}}{(A + B + S - nC_1 - C_2)^{n-4}} = \frac{C_1^2(A + B + S - nC_1 - C_2)^4}{(B - 2C_1 - C_2)^2(A - nC_1 - C_2)^4} \quad (7)$$

and taking the square root of both sides

$$k = \frac{C_1(A + B + S - nC_1 - C_2)^2}{(B - 2C_1 - C_2)(A - nC_1 - C_2)^2} \quad (8)$$

where.

$$k = \left[\frac{K_1(A - nC_1 - C_2)^{n-4}}{(A + B + S - nC_1 - C_2)^{n-4}} \right]^{1/2} \quad (9)$$

One then assumes a value of K_1 , substitutes the observed value of C_1 into eq. 9, solves for k , and then solves the cubic eq. 8 for C_1 . The process is repeated recalculating C_2 from eq. 6 and k each time until C_1 converges to a constant value; C_1 is thus known for the assumed value of K_1 . If values of C_1 for several samples are calculated in this manner for various values of K_1 , it is possible to choose a value of K_1 which best reproduces the observed value of C_1 over a range of A and B .

Values of C_1 may also be calculated for samples in which, owing to rapid exchange, C_1 is not measurable directly from the n.m.r. spectra. This is accomplished using the above procedure with the exception that only the previously determined value of K_1 (from spectra in which C_1 can be measured) is used and a reasonable value of C_1 is used in eq. 9 in place of the observed value of C_1 . The correct value of C_1 is then obtained by successive approximation as described above. In practice, the whole operation of calculating values of C_1 , C_2 , and K_1 was conveniently accomplished using the IBM 709 computer.

Mean Lifetimes and the Solution of the Modified Bloch Equations for the Special Three-Site Case, $A \rightleftharpoons B \rightleftharpoons C$. Following the treatments of Gutowsky⁵ and McConnell,⁶ the effect of chemical exchange will now be incorporated into the Bloch equations.⁷ Consider the system

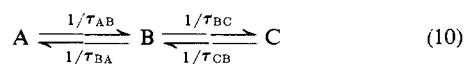
(4) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954).

(5) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(6) H. M. McConnell, *ibid.*, **28**, 430 (1958).

(7) F. Bloch, *Phys. Rev.*, **70**, 460 (1958).

(3) W. Finkelstein, *Z. physik. Chem.*, **124**, 285 (1926); H. Carlson, *Angew. Chem.*, **46**, 747 (1933); *Ber.*, **68B**, 2209 (1935); M. T. Uschakow, *ibid.*, **68B**, 824 (1935).



where A, B, and C represent magnetically different environments in which a nucleus engaging in chemical exchange may exist. The exchange reactions are limited to those between sites A and B and between sites B and C, excluding those between A and C directly, or $1/\tau_{AC} = 1/\tau_{CA} = 0$, where $1/\tau_{ij}$ represents the constant probability per unit time of the nucleus making a jump from site i to site j . Let us further consider the transverse relaxation times of the nuclei in the absence of exchange to be large, or

$$1/T_{2A} = 1/T_{2B} = 1/T_{2C} = 0 \quad (11)$$

where T_{2i} is the transverse relaxation time of the nucleus in site i in the absence of exchange. Let us define

$$\begin{aligned} 1/\tau_A &= 1/\tau_{AB} & \alpha &= 1/\tau_A - i\Delta\omega_A \\ 1/\tau_B &= 1/\tau_{BA} + 1/\tau_{BC} & \beta &= 1/\tau_B - i\Delta\omega_B \\ 1/\tau_C &= 1/\tau_{CB} & \gamma &= 1/\tau_C - i\Delta\omega_C \end{aligned} \quad (12)$$

where $\Delta\omega_j = \omega_j - \omega$, and ω_j is the Larmor precession frequency of the j nucleus in the absence of exchange.

The differential equations for the rates of change of the complex moments G_j for the three sites are

$$\begin{aligned} \frac{dG_A}{dt} + \alpha G_A &= -i\gamma H_1 M_0^A + \frac{G_B}{\tau_{BA}} \\ \frac{dG_B}{dt} + \beta G_B &= -i\gamma H_1 M_0^B + \frac{G_A}{\tau_A} + \frac{G_C}{\tau_C} \\ \frac{dG_C}{dt} + \gamma G_C &= -i\gamma H_1 M_0^C + \frac{G_B}{\tau_{BC}} \end{aligned} \quad (13)$$

The steady-state solution to the differential equations follows by setting $dG_j/dt = 0$ and solving the resulting simultaneous linear equations for the imaginary part of G , where

$$G = G_A + G_B + G_C = u + iv \quad (14)$$

since the n.m.r. spectrometer is tuned to respond to the imaginary part of the total complex moment, G . If we let $M_0^j = M_0 P_j$, then G is given by the expression

$$\begin{aligned} G = i\gamma H_1 M_0 \left[-P_A \left(\beta\gamma - \frac{1}{\tau_{BC}\tau_C} \right) - \frac{P_A\gamma}{\tau_C} - \right. \\ \left. \left(\gamma P_B + \frac{P_C}{\tau_C} \right) \left(\alpha + \frac{1}{\tau_{BA}} \right) - \alpha \left(\beta P_C + \frac{P_C}{\tau_{BC}} \right) + \right. \\ \left. \frac{1}{\tau_A} \left(\frac{P_C}{\tau_{BA}} - \frac{P_A}{\tau_{BC}} \right) \right] / \left[\alpha(\beta\gamma - 1/\tau_{BC}\tau_C) - \gamma/\tau_{BA}\tau_A \right] \end{aligned} \quad (15)$$

and the absorption mode, ν , is then obtained by rationalizing the denominator and retaining only the imaginary part of the resulting expression

$$\nu = \gamma H_1 M_0 \frac{RP - SQ}{P^2 + Q^2} \quad (16)$$

where

$$\begin{aligned} P &= \frac{\Delta\omega_B\Delta\omega_C}{\tau_A} - \frac{\Delta\omega_A\Delta\omega_C}{\tau_B} - \frac{\Delta\omega_A\Delta\omega_B}{\tau_C} \\ Q &= \frac{\Delta\omega_A}{\tau_C\tau_{BA}} - \Delta\omega_A\Delta\omega_B\Delta\omega_C - \frac{1}{\tau_A} \left(\frac{\Delta\omega_C}{\tau_{BC}} + \frac{\Delta\omega_B}{\tau_C} \right) \\ R &= -\frac{1}{\tau_C} \left(\frac{1}{\tau_A} + \frac{1}{\tau_{BA}} \right) + P_A\Delta\omega_B\Delta\omega_C + \\ &\quad P_B\Delta\omega_C\Delta\omega_A + P_C\Delta\omega_A\Delta\omega_B - \frac{1}{\tau_A\tau_{BC}} \end{aligned}$$

$$S = (P_B + P_C)(1/\tau_C + 1/\tau_{BC})\Delta\omega_A +$$

$$\begin{aligned} \frac{P_C}{\tau_{BA}}\Delta\omega_A + (P_A + P_B) \left(\frac{1}{\tau_A} + \frac{1}{\tau_{BA}} \right) \Delta\omega_C + \\ \frac{P_A}{\tau_{BC}}\Delta\omega_C + \left(\frac{P_A}{\tau_C} + \frac{P_C}{\tau_A} \right) \Delta\omega_B \end{aligned}$$

If we define

$$\frac{1}{\tau} = \frac{1}{\tau_A} + \frac{1}{\tau_{BA}} \quad \frac{1}{\tau'} = \frac{1}{\tau_C} + \frac{1}{\tau_{BC}} \quad (17)$$

and utilize the expressions

$$\begin{aligned} \tau_A &= \frac{P_A + P_B}{P_B} \tau & \tau_C &= \frac{P_B + P_C}{P_B} \tau' \\ \tau_{BA} &= \frac{P_A + P_B}{P_A} \tau & \tau_{BC} &= \frac{P_B + P_C}{P_C} \tau' \end{aligned} \quad (18)$$

we can simplify eq. 16 by neglecting terms in τ' with respect to those in τ . This assumption is for the case of exchange between sites B and C being much faster than the exchange between sites A and B, or $\tau \gg \tau'$, and, as will be discussed later, is applicable in the present investigation. Equation 16 then becomes

$$\begin{aligned} \nu = \left\{ -\gamma H_1 M_0 \frac{P_A}{P_A + P_B} D + [(P_B + P_C)^2 \Delta\omega_A + \right. \\ \left. P_A P_C \Delta\omega_C + P_A P_B \Delta\omega_B] F \right\} / \\ \left[\tau D^2 + \frac{F^2}{\tau} \right] \end{aligned} \quad (19)$$

$$D = -\Delta\omega_A(P_B\Delta\omega_B + P_C\Delta\omega_C)$$

$$F = \frac{P_A}{P_A + P_B} [P_A\Delta\omega_A + P_B\Delta\omega_B + P_C\Delta\omega_C]$$

Equation 19 predicts two peaks for large values of τ ; corresponding to slow exchange, centered on the frequencies

$$\omega = \omega_A \quad (20)$$

and

$$\omega = \frac{P_B\omega_B + P_C\omega_C}{P_B + P_C} \quad (21)$$

The equation predicts one peak for small values of τ , corresponding to rapid exchange, centered on the frequency

$$\omega = P_A\omega_A + P_B\omega_B + P_C\omega_C \quad (22)$$

Equation 19 may be rewritten in terms of a single variable, $\Delta\omega_B$, if one makes use of the relationships

$$\Delta\omega_C = \Delta\omega_B + (\omega_C - \omega_B) \quad (23)$$

$$\Delta\omega_A = \Delta\omega_B + (\omega_A - \omega_B)$$

Equation 19 then becomes

$$v = -\gamma H_1 M_0 \left[\left(\frac{P_A}{P_A + P_B} \right) R + (P_B + P_C) \Delta\omega_B L + \frac{(P_B + P_C)^2 (\omega_A - \omega_B) L + P_A P_B (\omega_C - \omega_B) L}{\left(\tau R^2 + \frac{L^2}{\tau} \right)} \right] \quad (24)$$

$$R = -(\Delta\omega_A + \omega_A - \omega_B) [(P_B + P_C) \Delta\omega_B + P_C (\omega_C - \omega_B)]$$

$$L = \frac{P_B}{P_A + P_B} [\Delta\omega_B + P_A (\omega_A - \omega_B) + P_C (\omega_C - \omega_B)]$$

Equation 24 is applicable to the system 2,4,6-trimethylpyridine (TMP)-iodine-nitrobenzene which contains the species $(\text{TMP})_2\text{I}^+$, free TMP, and $(\text{TMP})\text{I}_2$

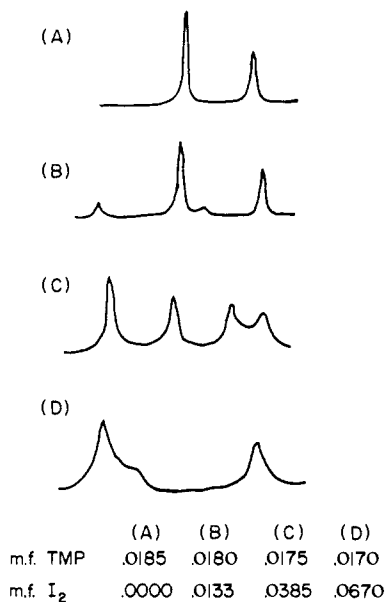


Figure 1. Spectra of 2,4,6-trimethylpyridine (TMP) in nitrobenzene solution showing the effect of adding iodine. Only the methyl resonance is shown.

and which will be discussed later in this paper. If we now let P_A , P_B , and P_C be the proton fractions of $(\text{TMP})_2\text{I}^+$, free TMP, and $(\text{TMP})\text{I}_2$, respectively, the observed n.m.r. spectrum of any sample may then be reproduced by calculating C_1 and C_2 as previously de-

scribed and plotting eq. 24, employing τ as a parameter until the best fit of the observed spectrum is obtained. From the value of τ , the value of τ_A may be calculated from eq. 18.

Experimental

The iodine, tetramethylsilane, nitrobenzene, and carbon tetrachloride were obtained and purified as previously described.⁸ 2,4,6-Trimethylpyridine (Eastman Organic Chemicals) was distilled shortly before use.

The n.m.r. samples were prepared and observed as previously described.⁸ The n.m.r. spectra were recorded using a Varian Associates, Inc., HR spectrometer operating at 60 Mc./sec.

The TMP-iodine equilibrium was studied in three solvent mixtures in which the weight ratios of nitrobenzene to carbon tetrachloride were 1:0, 3:1, and 1:1. Each solvent mixture contained 1% tetramethylsilane as an internal n.m.r. reference. Samples were prepared from each of the three solvent mixtures with approximately 0.02 m.f. of TMP and an iodine concentration between 0 and 0.07 m.f. Electron spin resonance by these samples was not detectable.

Results

The TMP exhibits two peaks in the methyl region, with an intensity ratio of 2:1. These peaks are attributable to the α -methyl and γ -methyl protons. Upon addition of iodine to the TMP solutions, two

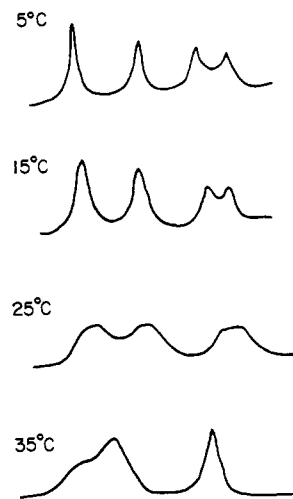


Figure 2. Spectra of TMP in nitrobenzene solution showing the effect of raising the temperature. Only the methyl resonance is shown. M.f. of 2,4,6-trimethylpyridine, 0.0175; m.f. of iodine, 0.0385; m.f. of nitrobenzene, 0.9440.

additional peaks are observed in the methyl region, having an intensity ratio of 2:1. The latter pair of peaks increases in intensity as the iodine concentration is increased and also as the temperature is lowered. With the increase in intensity of the new peaks, the original peaks are observed to decrease in intensity. Each new peak decreases in intensity, becomes broader, and eventually merges with the corresponding original

(8) D. W. Larsen and A. L. Allred, *J. Am. Chem. Soc.*, **87**, 1216 (1965).

methyl peak as the temperature of the system is raised, so that at high temperatures only two slightly broadened peaks are observed in the methyl region, with an intensity ratio of 2:1. Their positions, however, are shifted relative to those of the peaks observed in the absence of added iodine.

Spectra illustrating the behavior of the methyl resonance of the TMP-iodine system in nitrobenzene are shown in Figures 1 and 2. Chemical shifts of the α -methyl peaks are given in Table I. After recording the

greatly broadened, eq. 24 predicts two maxima at positions essentially those given by eq. 20 and 21.

The value of $(\omega_A - \omega_B)$ will then be given by $2\pi(\delta_1 + 145.0)$ radians/sec., and the value of $(\omega_C - \omega_B)$ will be given by $2\pi[\delta_2(P_B + P_C)/P_C - P_B\omega_B/2\pi P_C + 145.0]$ radians/sec. measured in spectra where the peaks are not greatly broadened owing to exchange. In these solutions, the equilibrium constants are so large that there is very little free base with respect to 1:1 complexed base, or $P_C \gg P_B$, so that $(\omega_C - \omega_B) i_s$

Table I. Chemical Shifts in C.p.s. of the α -Methyl Peaks Relative to Tetramethylsilane for the TMP-Iodine System in Nitrobenzene-Carbon Tetrachloride Solutions^a

Sample no.	TMP, m.f.	I ₂ , m.f.	Nitrobenzene, m.f.	5°		15°		25°		35°	
				δ_1	δ_2	δ_1	δ_2	δ_1	δ_2	δ_1	δ_2
1	0.0183	0.0000	0.9817		-145.5		-145.0		-144.3		-145.3
2	0.0180	0.0133	0.9687	-162.4	-146.0			-165.3	-146.4		
3	0.0170	0.0242	0.9588			-162.9	-148.7	-164.7	-150.3	-163.6	-150.9
4	0.0168	0.0328	0.9504			-164.2	-151.1	-163.2	-150.8		
5	0.0175	0.0385	0.9440	-164.1	-153.4	-165.9	-153.9	-165.4	-154.3	-161.6	-161.6
6	0.0165	0.0508	0.9327			-162.1	-155.7	-162.1	-162.1	-162.6	-162.6
7	0.0170	0.0670	0.9160	-168.1	-161.3	-166.0	-166.0	-162.7	-162.7	-163.9	-163.9
8	0.0190	0.0000	0.7721		-144.3		-143.4		-144.5		-145.3
9	0.0192	0.0359	0.7460			-166.8	-157.0	-165.9	-155.9	-156.7	-156.7
10	0.0181	0.0424	0.7411	-168.0	-153.8	-166.6	-156.2	-166.1	-156.3	-157.5	-157.5
11	0.0189	0.0513	0.7342			-163.7	-163.7	-161.9	-161.9	-161.8	-161.8
12	0.0174	0.0755	0.7160	-166.1	-157.5	-166.5	-166.5	-163.9	-163.9	-164.8	-164.8
13	0.0212	0.0000	0.5432		-143.1		-141.7		-142.9		-142.4
14	0.0206	0.0191	0.5330	-168.8	-152.3		-150.9		-149.5		-149.7
15	0.0203	0.0346	0.5256	-170.4	-153.6	-169.4	-154.4	-164.9	-152.5	-153.5	-153.5
16	0.0195	0.0699	0.5051	-172.2	-160.5	-170.7	-170.7	-164.9	-164.9	-164.4	-164.4

^a δ_1 is the chemical shift of the new complex peaks observed upon addition of iodine, and δ_2 is the chemical shift corresponding to the original peak.

spectra of the equilibrium mixtures at 35°, the spectra were again recorded at 5° to see if evidence of a chemical reaction could be found. The spectra were identical with those observed earlier at 5°, and the peaks were observed to increase or decrease in intensity with change in temperature in a manner which is consistent with that of a reversible system.

The new peaks (at δ_1) observed upon addition of iodine to the system can be attributed to an ionic complex of the type mentioned previously. The peaks (at δ_2), which upon addition of iodine to the TMP system appear at positions slightly shifted from that of the free base, can be attributed to a complex of the 1:1 type undergoing rapid exchange with free base.

The values of $(\omega_A - \omega_B)$ and $(\omega_C - \omega_B)$ must be determined for use in eq. 24 before a value of τ_A can be estimated, and the line shapes predicted by eq. 24 show that these estimates can be made directly from the observed spectra in certain instances. In any sample where ionic complex, 1:1 complex, and free base are exchanging in the manner described previously, the equation for the line shape predicts a gradual change from two sharp, distinct peaks to two broad peaks and finally to one merged peak as the rate of exchange between ionic complex and free base is increased. The positions of the peak maxima predicted by the equation are not appreciably displaced toward one another from their positions in the absence of exchange until the value of the exchange rate is raised sufficiently to predict two rather broad lines. Thus, if the rate of exchange is such that the peaks are not

given by $2\pi(\delta_2 + 145.0)$ radians/sec. The average values of $(\omega_A - \omega_B)$ and $(\omega_C - \omega_B)$ for the three solvents are shown in Table II.

Table II. Average Value of $(\omega_A - \omega_B)$ and $(\omega_C - \omega_B)$ in Radians/Sec. for the TMP-Iodine System in Mixtures of Nitrobenzene and Carbon Tetrachloride

Ratio C ₆ H ₅ NO ₂ :CCl ₄	$(\omega_A - \omega_B)$	$(\omega_C - \omega_B)$
1:0	-118.1	-56.5
3:1	-138.8	-75.5
1:1	-153.9	-81.8

The form $(\text{TMP})_2\text{I}^+ + \text{I}_3^-$, or $n = 5$, was found to give the best fit of the observed intensity data. The presence of ions of this type has been reported elsewhere and will be reviewed in the Discussion section. Using this equilibrium form and the method outlined previously, values of P_A , P_B , and P_C were calculated. The values of K_1 which gave the best fit of the data are shown in Table III, and the observed and calculated values of P_A are shown in Table IV along with calculated values of P_B . Using the values of K_1 shown in Table III, a least-squares treatment of a plot of $\log K_N$ vs. $1/T$ gave the values of ΔH and ΔS presented in Table V.

The values determined for P_A , P_B , and P_C were substituted into eq. 24, and the theoretical line shapes were

Table III. Values of K_1 (m.f.)⁻⁵ and K_2 (m.f.)⁻¹ for the TMP-Iodine System in Nitrobenzene-Carbon Tetrachloride Solution

Ratio C ₆ H ₅ NO ₂ :CCl ₄	5°	15°	25°	35°
K_1 (1:0)	3×10^{13}	9×10^{12}	2×10^{12}	1×10^{11}
K_1 (3:1)	9×10^{12}	3×10^{12}	1×10^{12}	8×10^{10}
K_1 (1:1)	2×10^{12}	5×10^{11}	1×10^{11}	...
K_2	5×10^3	3×10^3	2×10^3	1.2×10^3

calculated employing τ as a parameter. Included in the output of the IBM 709 computer were plots of calculated curves for various τ -values. The values of τ which gave the theoretical curves best fitting the observed spectra were then determined, and values of τ_A were then calculated from eq. 18 and are presented in Table IV.

Discussion

The existence of polyhalide ions in various solvents has been demonstrated, and evidence has been obtained for the existence of polyiodide ions as large as I_{11}^- .⁹ Awtrey and Connick¹⁰ have demonstrated the existence of I_3^- ions in water and have measured a concentration dissociation constant, K_C , of 1.4×10^{-3} at 25° for the equilibrium $I_3^- \rightleftharpoons I_2 + I^-$. The heat of formation of the triiodide ion was found to be -12.72 kcal./mole.¹¹

Popov and Rygg¹² have observed the presence of IBr_2^- and ICl_2^- ions in solutions of complexes of the type 2,6-lutidine-IX in acetonitrile. They attribute the presence of IX_2^- ions to equilibria of the type $2B-IX \rightleftharpoons B_2I^+ + IX_2^-$ in solvents of high dielectric constant. They also found no evidence for IX_2^- ions in carbon tetrachloride solutions and postulated that equilibria of the type $B-IX \rightleftharpoons B + IX$ predominate in solutions of low dielectric constant. A value of K_C at 25° for complex dissociation of 1.97×10^{-2} is reported for the 2,6-lutidine-iodine complex in carbon tetrachloride solution. Conductivity studies¹³ indicate that definite but small amounts of "inner complex" are formed instantaneously upon dissolving iodine in pyridine.

Hassel, *et al.*,¹⁴ prepared a compound from alcohol solution which had the composition of 2 moles of iodine to 1 mole of pyridine. X-Ray analysis of this compound showed that the crystal lattice of the compound is built up of $\gamma\text{-pic-I}^+\text{-py}$ cations and I_3^- anions. It was also suggested¹⁴ that a previously reported¹⁵ compound, $(\gamma\text{-picoline})_2I_2$, should be assigned the structure $(\gamma\text{-pic-I-}\gamma\text{-pic})^+ + I_3^-$. Other amine-iodine complexes studied by Hassel^{2b} appear to be simple 1:1 linear complexes in which the iodine-iodine bond remains intact.

In view of the preceding paragraphs, the form assumed for the complex of TMP with iodine is not unreasonable in a solvent of high dielectric constant

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Table IV. Proton Fractions for Uncomplexed TMP (P_B) and for the Ionic Complex (P_A and P_A') and the Mean Lifetimes of the Ionic Complex

Ratio C ₆ H ₅ NO ₂ : CCl ₄	Sam- ple no.	5°		15°		25°		35°									
		P_A' obsd.	P_A calcd.	P_A' obsd.	P_A calcd.	P_A' obsd.	P_A calcd.	P_A' obsd.	P_A calcd.								
1:0	2	0.12	0.21	0.40	0.25	0.32	0.22	0.18	0.16	0.10	0.30	0.04	0.05	0.02	0.02	6 × 10 ⁻²	3 × 10 ⁻¹
	3			0.48	0.45	0.37	0.40			0.01	0.01					2	1 × 10 ⁻¹
	4	0.61	0.58	0.53	0.53	0.50	0.50			0.05	0.04					4 × 10 ⁻¹	1 × 10 ⁻¹
	5			0.64	0.66	0.62	0.62			0.04	0.04					4 × 10 ⁻¹	6 × 10 ⁻²
	6			0.45	0.38	0.01	0.01			0.40	0.37					4 × 10 ⁻¹	2 × 10 ⁻²
	9	0.59	0.57	0.49	0.51	0.45	0.40			0.45	0.40					2 × 10 ⁻²	3 × 10 ⁻¹
3:1	10															3 × 10 ⁻¹	1 × 10 ⁻¹
	11															3 × 10 ⁻¹	1 × 10 ⁻¹
1:1	12	0.77	0.77	0.01	0.01	0.01	0.01			0.01	0.01					6 × 10 ⁻²	6 × 10 ⁻²
	14	0.05	0.02	0.12	0.12	0.02	0.02			0.02	0.02					2 × 10 ⁻²	2 × 10 ⁻²
	15	0.36	0.28	0.01	0.01	0.01	0.01			0.02	0.02					3 × 10 ⁻¹	3 × 10 ⁻¹
	16	0.67	0.67	0.01	0.01	0.01	0.01			0.02	0.02					6 × 10 ⁻²	1 × 10 ⁻¹

Table V. Values of ΔH and ΔS for the Ionic Complex Formation (Reaction 3, $n = 5$) in the TMP-Iodine System in Nitrobenzene-Carbon Tetrachloride Solution

Ratio $C_6H_5NO_2: CCl_4$	ΔH , kcal./mole	ΔS , e.u.
1:0	-31.5 ± 3.8	-50.6 ± 13.1
3:1	-25.8 ± 3.2	-32.9 ± 10.9
1:1	-24.7 ± 1.0	-32.2 ± 3.6

Table VI. Observed Chemical Shifts for the TMP-Iodine System in Carbon Tetrachloride Solution at 25°

TMP, m.f.	0.0223	0.0223	0.0223	0.0222	0.0070	0.0070
I ₂ , m.f.	0.0000	0.0019	0.0041	0.0082	0.0150	0.0200
δ , c.p.s.	-143.0	-144.0	-145.4	-148.8	-156.6	-158.4

such as nitrobenzene. Additional evidence for the structure of the complex was obtained from an experiment in which a small amount of *n*-butylammonium iodide was added to a nitrobenzene solution containing TMP and iodine. The added iodide should complex the iodine and thus shift the equilibrium. The solution contained 0.0466 m.f. of iodine, 0.0236 of iodide ion, and 0.0178 of TMP. The n.m.r. absorption of complexed base was not observable. A calculation of the amount of complexed base predicted indicates that, if I₃⁻ ions were predominantly formed in the solution, about 32% of the base should be complexed, and that, if I₅⁻ ions or higher polyiodides were predominant, the complexed base would not be observable. This indicates a strong tendency for each I⁻ ion in solution to associate with two or more iodine molecules.

The observed variation in δ_2 , the position of the upfield α -methyl peak, upon addition of iodine to the system cannot be accounted for by proposing a simple equilibrium between ionic complex, of the type discussed above, and free base with chemical exchange reducing the observed peak separation, $\delta_1 - \delta_2$, between the two sharp peaks. The reason that this simple picture must be ruled out, as was previously stated, is that, as the exchange rate is gradually increased, considerable line broadening is observed before the chemical shift difference is appreciably reduced. This behavior is general and not a consequence of the original exchange form chosen in the derivation of eq. 24.

The observed variation of δ_2 with increasing iodine concentration can be accounted for by postulating a second type of complex other than the ionic complex, which gives rise to the peak at δ_1 . This second complex is presumably the 1:1 molecular complex most commonly formed between iodine and Lewis bases. To test this assumption, samples of TMP and iodine were prepared in carbon tetrachloride solution. The chemical shifts were measured relative to 1% tetramethylsilane internal reference, and chemical shifts are listed in Table VI. Carbon tetrachloride is a low dielectric constant solvent, and formation of ionic species would not be favored therein. The K_C value of 52.0 has been reported for the TMP-iodine complex formation¹⁶ at 28° in chloroform. This corresponds roughly to a K_N value of 500, from which an "association shift" may be calculated by an extrapolation of the data in

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Table VI. The "association shift" is approximately -17.5 c.p.s. in carbon tetrachloride solution, which indicates that the values of $(\omega_C - \omega_B)$ in Table II are reasonable and that the data are consistent with the proposed equilibria.

The variation of δ_2 with iodine concentration cannot be explained by an interaction of TMP with nitrobenzene even though complexes of nitrobenzene with

amines are known to exist and are known to have values of K_N between 1 and 10 for complex formation.^{17,18} The chemical shifts of 0.02 m.f. of TMP in solutions of the solvents TMP, carbon tetrachloride, and nitrobenzene, each containing 1% tetramethylsilane, were measured at 25° and found to be -141.3, -143.0, and -145.0 c.p.s., respectively. If K_N is 1 for complex formation, approximately 50% of the TMP would be complexed in nitrobenzene solution, and the extrapolated "association shift" of the TMP-nitrobenzene complex would be -3.8 c.p.s., which is far below the values of $(\omega_C - \omega_B)$ actually observed. The differences in chemical shifts of the TMP in various solvents can more probably be attributed to anisotropy effects.¹⁹

Keefer and Allen²⁰ have made an estimate of the tendency for self-association of the iodine molecules in carbon tetrachloride solution. They have estimated that the equilibrium constant, K_C , for the interaction $2I_2 \rightleftharpoons I_4$ lies between 0.5 and 0.05, which corresponds to a K_N value of about 1. Under the experimental conditions in this investigation, one would expect about 5% of the iodine in solution to exist as I₄. Thus, not including calculations for this interaction should not lead to any observable error in calculating concentrations of complex.

Plyler and Mulliken²¹ reported a K_C value of 200 at 26° for the formation of the py·I₂ complex in benzene. Reid and Mulliken⁴ studied the pyridine-iodine complex in *n*-heptane solution at 16.7° and report K_C values of 290, ΔH of -7.8 kcal./mole, and ΔS of -15.5 e.u. The data of Reid and Mulliken were used to estimate the value of K_2 for the TMP-iodine system rather than the data reported in ref. 16 since a value of ΔH was not reported by the latter authors.

The assumption that T_2 values are large does not lead to errors in the determination of τ -values since the observed lines are sharp and well separated when the exchange is slow. The widths of the lines will be determined largely by the values of T_2 in the case of very slow exchange, but, when the exchange rate is intermediate, as in the present investigation, the line shapes

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Table VII. Calculated Values of $\tau_A P_B$ and Values of Free Base Proton Fraction for the TMP-Iodine System in Nitrobenzene-Carbon Tetrachloride Solution

Ratio C ₆ H ₅ NO ₂ : CCl ₄	Sample no.	5°		15°		25°		35°	
		$\tau_A P_B$	P_B	$\tau_A P_B$	P_B	$\tau_A P_B$	P_B	$\tau_A P_B$	P_B
1:0	2	4×10^{-2}	0.48	3×10^{-2}	0.48
	3	4×10^{-2}	0.01	2×10^{-2}	0.01	3×10^{-2}	0.10
	4	1×10^{-1}	0.02	2×10^{-2}	0.05
3:1	5	3×10^{-1}	0.01	1×10^{-1}	0.02	2×10^{-2}	0.04	4×10^{-3}	0.04
	6	4×10^{-3}	0.02
	9	5×10^{-2}	0.01	4×10^{-3}	0.01	3×10^{-3}	0.05
1:1	10	1×10^{-1}	0.01	6×10^{-2}	0.03	6×10^{-4}	0.03
	11	3×10^{-2}	0.01	6×10^{-3}	0.02	2×10^{-3}	0.02
	12	8×10^{-3}	0.01	3×10^{-3}	0.01	1×10^{-3}	0.02
1:1	14	4×10^{-3}	0.12
	15	4×10^{-2}	0.01	2×10^{-2}	0.01	3×10^{-3}	0.04
	16	4×10^{-3}	0.01	3×10^{-3}	0.01	2×10^{-3}	0.03

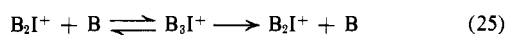
will not depend upon T_2 values as long as they are large.

The assumption that $\tau \gg \tau'$ may be justified by the following considerations. From the data given in Table VI, an "association shift" of -17.5 c.p.s. (-110.0 radians/sec.) is estimated. This value agrees well with the values of $(\omega_C - \omega_B)$ in Table II. Since no line broadening owing to exchange was detected in the system shown in Table VI, we may set a lower limit upon τ' by use of the equation⁸

$$\frac{1}{T_2'} = \frac{P_B}{T_{2B}} + \frac{P_C}{T_{2C}} + P_B^2 P_C^2 (\omega_C - \omega_B)^2 (\tau_B + \tau_C)$$

For $(\omega_C - \omega_B) = -110.0$ radians/sec., $\tau' \leq 3 \times 10^{-4}$ sec., which is much less than the values of τ_A shown in Table IV.

Two mechanisms will be considered for the exchange.



and



for which the rate expressions may be written

$$\frac{dP_A}{dt} = -k_A P_A P_B \quad (27)$$

and

$$\frac{dP_A}{dt} = -k'_A P_A \quad (28)$$

Since the value of τ_A is the reciprocal of the pseudo-first-order rate constant, mechanism 25 predicts that

τ_A is dependent upon P_B , and mechanism 26 indicates that τ_A is independent of P_B . Values of τ_A in Table IV appear to have a dependence on P_B , and values of $\tau_B P_B$, as shown in Table VII, appear to be independent of P_B although there is some experimental scattering of the values. The data appear to be consistent with mechanism 25 but, of course, do not establish that mechanism. Average values of the rate constants for complex exchange, as defined by eq. 27 and by $k_A = 1/P_B \tau_A$, are presented in Table VIII.

Table VIII. Values of the Rate Constants [(m.f.)⁻¹ sec.⁻¹] for the Ionic Complex Exchange in the TMP-Iodine System in Nitrobenzene-Carbon Tetrachloride Solution

Ratio C ₆ H ₅ NO ₂ : CCl ₄	5°	15°	25°	35°
1:0	5	2×10	5×10	1×10^2
3:1	2×10	3×10	3×10^2	4×10^2
1:1	5×10	1×10^2	5×10^2	...

Acknowledgments. D. W. L. expresses appreciation for a Woodrow Wilson Fellowship, a fellowship from the Lubrizol Corp., and a predoctoral fellowship from the Division of General Medical Sciences, United States Public Health Service. We thank the Northwestern University Computing Center for providing computer time. The research upon which this report is based was partially supported by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center.